

# Onion structures induced by hydrophilic and hydrophobic ions in a binary mixture

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Phase transition is observed between one-phase disordered phase and an ordered phase with multi-lamellar (onion) structures in an off-critical mixture of  $D_2O$  and 3-methylpyridine (3MP) containing a salt at 85mM. The salt consists of hydrophilic cations and hydrophobic anions, which interact asymmetrically with the solvent composition fluctuations inducing mesophases. The structure factor of the composition distribution obtained from small-angle neutron scattering has a peak at an intermediate wave number in the disordered phase and multiple peaks in the ordered phase. Lamellar layers forming onions are composed of solvation-induced charged membranes swollen by  $D_2O$ . The onion phase is realized only for small volume fractions of 3MP (in  $D_2O$ -rich solvent).

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Binary mixtures of water and organic solvent have been used extensively to study universal aspects of critical behavior and phase separation dynamics. However, not enough attention has yet been paid to unique ion effects in such mixtures, where preferential hydration around each ion should affect the composition fluctuations [1, 2]. Salts composed of small hydrophilic ions can drastically change the phase behavior even at small concentrations [3, 4, 5, 6, 7]. More strikingly, many groups have observed long-lived heterogeneities (sometimes extending over a few micrometers) in one-phase state [8, 9] and a third phase visible as a thin plate formed at a liquid-liquid interface in two-phase state [10]. These observations were reproduced in different experiments using solvents and salts of high purity, so they should be regarded as ion-induced supramolecular aggregates. We also comment on a mixture of water+isobutylic acid (IA), where IA partly dissociates into  $H^+$  and Butyrate $^-$  ions. There, the mobility of  $H^+$  ions much decreases at large IA contents in one-phase state [11] and the third phase also appears around an interface in two-phase state [10]. Similar phenomena have often been observed in various soft matters such as polymers, gels, colloids, and mixtures containing surfactants. Though not well understood, the solvation (ion-dipole) interaction among ions and polar molecules should play a major role in these phenomena together with the Coulombic interaction among charges. [1, 2]

Recently, the solvation effect on phase behavior was

theoretically studied in polar mixtures including the case of antagonistic ion pairs composed of hydrophilic and hydrophobic ions [12]. Such cations and anions interact differently with the composition fluctuations, leading to a charge-density-wave phase for sufficiently large solvation asymmetry even at small salt concentrations. In a small-angle neutron scattering (SANS) experiment, Sadakane *et al.* [13] found a peak at an intermediate wave number  $Q_m (\sim 0.1 \text{ \AA}^{-1})$  in a near-critical mixture of  $D_2O$  and 3-methylpyridine (3MP) containing sodium tetraphenylborate  $NaBPh_4$  at 100 mM. The volume fraction of 3MP, denoted by  $\phi_{3MP}$ , was chosen to be 0.35, 0.42, and 0.54. This salt dissociates into hydrophilic  $Na^+$  and hydrophobic  $BPh_4^-$ . The  $BPh_4^-$  is composed of four phenyl rings bonded to an ionized boron. This anion acquires strong hydrophobicity such that the salt is more soluble to pure 3MP than to pure  $D_2O$  despite the hydrophilic nature of  $Na^+$  [14]. Furthermore, the mixture exhibited colors changing dramatically on approaching the criticality at low salt concentrations ( $\sim 10$  mM), indicating emergence of large scale heterogeneities. No distinct mesophases appeared in the same solvent when hydrophilic salts such as  $NaCl$  were added [15].

In this Letter, we again use the system of  $D_2O$ +3MP+ $NaBPh_4$ . We purchased  $D_2O$  with isotopic purity of 99% from EURISO-TOP and 99% 3MP and 99.5 %  $NaBPh_4$  from Aldrich. These chemicals were mixed without further purification. As a new finding, we report observation of multi-lamellar (onion) structures for small  $\phi_{3MP}$ . Detailed measurements were made for  $\phi_{3MP} = 0.08, 0.09, 0.11$ , and  $0.14$  in the temperature range  $283 \text{ K} \leq T \leq 343 \text{ K}$ . The concentration of

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NaBPh<sub>4</sub> was fixed at 85 mM. In this mixture solvent, there is a lower critical solution temperature (LCST) at 310 K for  $\phi_{3MP} = 0.30$ . Without salt, the mixtures of the same composition as our systems are homogeneous in this temperature range, and the composition fluctuation is very small. However, with addition of NaBPh<sub>4</sub>, onions appeared spontaneously directly from disordered states. If  $\phi_{3MP} = 0.09$  as an example, the ratios among the number densities of D<sub>2</sub>O, 3MP, and NaBPh<sub>4</sub>, denoted by  $n_D$ ,  $n_{3MP}$ , and  $n_{salt}$ , are given by

$$n_D/n_{3MP} \cong 54.3, \quad n_{3MP}/n_{salt} \cong 10.9. \quad (1)$$

Thus  $n_{salt} \ll n_{3MP} \ll n_D$ . The molecular volumes of D<sub>2</sub>O and 3MP (the inverse densities of the pure components) are 28 and 168 Å<sup>3</sup>, respectively. The volume fraction of NaBPh<sub>4</sub> was less than 2 % and the observed SANS intensity was mostly due to the composition distribution of the solvent. Also in surfactant mixtures, the spontaneous onion formation (without applying shear flow) has been observed at small surfactant concentrations in water-rich solvent [16, 17, 18, 19].

Figure 1 gives temperature dependence of optical microscopic images. These images were taken using a Nikon Optiphot2-Pol with a CCD camera. The thickness of the sample was 90 μm and the temperature of the samples was controlled within an accuracy better than 0.1 K using a Linkam TH-99 hot stage. The composition of the sample was  $\phi_{3MP} = 0.09$ . At  $T = 323$  K (Fig. 1 (a)), the whole area is homogeneous without visible structures. As we decreased  $T$  below 318 K, small droplets emerged from the whole sample and grew in size. (Fig. 1 (b)). In (c),  $T$  is further lowered to 293 K and the space is nearly filled with deformed droplets with diameter about 20 μm. The left panel of (b') gives a magnified picture of (b), while the right panel is the corresponding Maltese cross pattern obtained by crossed Nicoles under polarized light. This pattern arises from inhomogeneous composition distributions with spherical symmetry. Such patterns have been observed for polymer spherulites [20] and onions of surfactant systems [17, 18, 19]. Thus our result indicates that the onion structure is formed below  $T_L$ , where  $T_L = 318$  K is the transition temperature.

SANS experiments were performed at SANS-J, JRR-3M in Japan Atomic Energy Agency. A 6.0 Å incident neutron beam was mechanically selected with a wavelength resolution of 13 %, and the scattered neutrons were detected at 2.5 m and 10 m from the sample position. Each sample was kept in a quartz cell of 2 mm thickness and placed in a temperature-controlled chamber with an accuracy better than 0.1 K. The measured wave number  $Q$  ranged between  $6 \times 10^{-3}$  Å<sup>-1</sup> and  $1.3 \times 10^{-1}$  Å<sup>-1</sup> and the observed two-dimensional data were azimuthally averaged. Figure 2 displays the SANS intensity vs  $Q$  from the sample of  $\phi_{3MP} = 0.09$ . With varying  $T$ , the system was in the disordered phase for  $T > T_L$  and in the ordered phase for  $T < T_L$ . At the lowest temperature 283 K in Fig. 2, a Bragg peak is pronounced at  $Q_m = 3.4 \times 10^{-2}$  Å<sup>-1</sup>, the second one

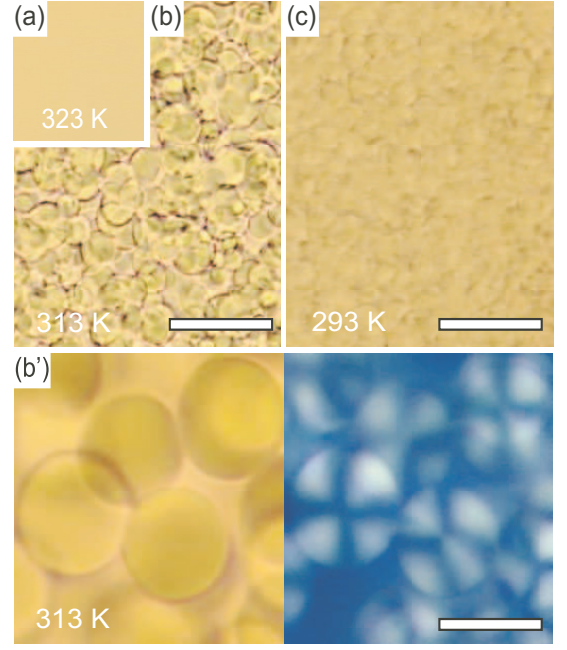


FIG. 1: Optical microscopic images obtained from the sample of  $\phi_{3MP} = 0.09$ ; (a)  $T = 323$  K (disordered), (b)  $T = 313$  K (onion), and (c)  $T = 293$  K (onion). Scale bars in (b) and (c) indicate 100 μm. (b') A magnified image of (b) (left) and a birefringent image of the same region (right) with scale bar being 20 μm.

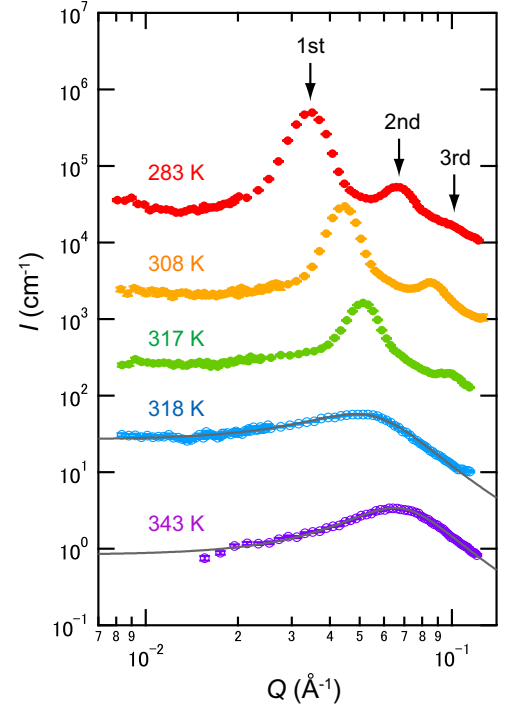


FIG. 2: Temperature dependence of SANS intensity from a sample of  $\phi_{3MP} = 0.09$ . First-order transition occurs slightly below  $T = 318$  K. Data at lower temperatures are shifted by multiplying 10 from below.

appears at  $6.8 \times 10^{-2} \text{ \AA}^{-1}$ , and a slight shoulder exists around  $1.02 \times 10^{-1} \text{ \AA}^{-1}$  (though not clearly seen in the figure). The same behavior was found for all the SANS data below  $T_L$ , demonstrating the formation of aligned lamellae. This is another evidence of the onion formation below  $T_L$ .

In the disordered phase above  $T_L$ , the intensity exhibits a broad peak at  $Q_m \sim 0.07 \text{ \AA}^{-1}$ , with  $Q_m$  slightly shifting to lower values as  $T \rightarrow T_L$ . It may fairly be fitted to the theoretical mean-field intensity  $I_{OK}(Q)$  (solid curves for  $T = 343$  and  $318$  K in Fig. 2) [12]. Its inverse is of the form

$$I_{OK}(0)/I_{OK}(Q) = 1 + \left[ 1 - \frac{\gamma_p^2}{1 + \lambda^2 Q^2} \right] \xi^2 Q^2, \quad (2)$$

where  $\gamma_p$  represents the degree of solvation asymmetry between cations and anions. For  $\gamma_p = 0$  it follows the Ornstein-Zernike form. For  $\gamma_p > 1$  the structure factor has a peak at an intermediate wave number. In the present case  $\gamma_p$  is taken as an adjustable parameter given by 2.32 at  $T = 333$  K and by 1.96 at  $T = 320$  K. Slightly below  $T_L$ , the system was phase-separated into an ordered phase in an upper region and the disordered phase in a lower region. The data in the case  $T < T_L$  in Fig. 2 are those from the upper region. The transition is thus first-order. In addition, the same  $T_L$  was obtained with decreasing and increasing  $T$  around the transition. The mass density of  $D_2O$  is  $1.11 \text{ g/cm}^3$  and that of 3MP is  $0.96 \text{ g/cm}^3$ , so the lighter ordered phase contains more 3MP than the coexisting disordered phase. In this case the mass density difference between the two phases is less than  $10 \text{ mg/cm}^3$ . As  $T$  was further lowered, the onion droplets became more swollen by  $D_2O$ . This results in an increase of the lamellar spacing, as will be shown in Fig. 3. At low temperatures below  $293$  K, the whole cell was filled with swollen onions.

The lamellar/disorder transition occurred only in a window composition range  $0.05 < \phi_{3MP} < 0.12$ . Figure 3 shows the temperature dependence of the mean repeat distance  $d = 2\pi/Q_m$  calculated from the peak position  $Q_m$ . For  $\phi_{3MP} = 0.09$ ,  $d$  considerably increases with decreasing  $T$  in the range  $293 \text{ K} < T < T_L$ , which is due to the swelling of the onions. The relaxation time of this swelling was shorter than 1 min. For  $\phi_{3MP} = 0.14$ ,  $d$  varies very weakly in the whole temperature range. Above  $330$  K,  $\phi_{3MP}$  dependence of  $d$  is weak. The transition temperature  $T_L$  decreases with increasing  $\phi_{3MP}$ , being equal to  $318$  K and  $303$  K for  $\phi_{3MP} = 0.09$  and  $0.11$ , respectively. However, the system remained in the disordered phase for  $\phi_{3MP} \geq 0.14$ . The figure indicates that the transition occurs for  $d \sim 130 \text{ \AA}$ .

Figure 4 shows a ultra small-angle neutron scattering (USANS) spectrum observed at PNO spectrometer in JRR-3M ( $2 \times 10^{-5} < Q < 5 \times 10^{-4} \text{ \AA}^{-1}$ ) together with the data obtained at SANS-J in focusing-SANS mode (the lowest- $Q$  is expanded down to  $3 \times 10^{-4} \text{ \AA}^{-1}$  [21]). The measurement was done at  $T = 298$  K for the sam-

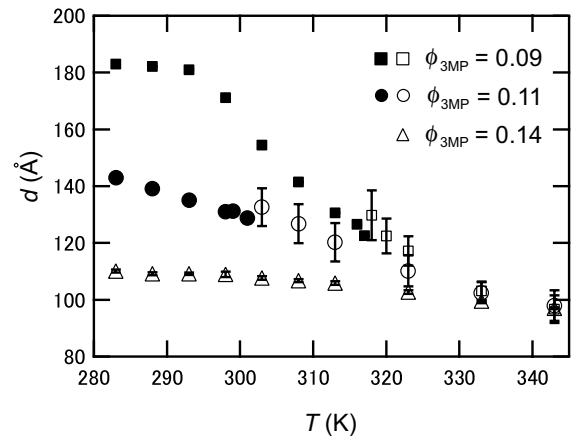


FIG. 3: Repeat distance  $d = 2\pi/Q_m$  vs temperature  $T$  for  $\phi_{3MP} = 0.14$  (triangle),  $0.11$  (circle), and  $0.09$  (square). Open symbols are data in the disordered phase, while filled symbols in the onion phase. No onion appears for  $\phi_{3MP} = 0.14$ .

ple of  $\phi_{3MP} = 0.09$ . The low- $Q$  profile obeys the Porod law in the range of  $1 \times 10^{-4} < Q < 5 \times 10^{-3} \text{ \AA}^{-1}$ . It should arise from the interfaces of the onion droplets in the range  $R^{-1} \ll Q \ll Q_m$ , where  $R$  is the droplet radius. Each onion is composed of about 1000 concentric lamellae provided if the droplet interior is filled with lay-

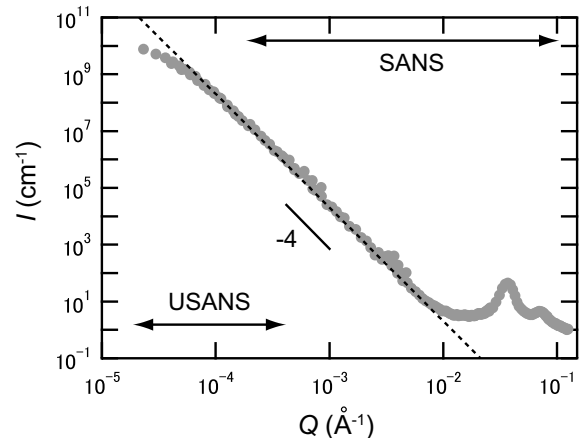


FIG. 4: Connected USANS profile obtained at PNO and SANS-J over a wide range of  $Q$  at  $T = 298$  K and  $\phi_{3MP} = 0.09$ . The Porod tail  $\propto Q^{-4}$  from onion surfaces can be seen in the range  $1 \times 10^{-4} < Q < 5 \times 10^{-3} \text{ \AA}^{-1}$ .

Now we discuss the physical processes involved. In aqueous solutions, each  $Na^+$  ion is known to be surrounded by a hydration shell composed of several water molecules [1, 2]. This then suggests that each  $BPh_4^-$  ion should be solvated by a certain number of 3MP molecules around it due to its strong hydrophobicity [14], though we do not know this solvation number  $N_{3MP}^s$  at present. See eq. (1) for the average number densities of  $BPh_4^-$

and 3MP,  $n_{\text{salt}}$  and  $n_{\text{3MP}}$ , as typical values in the disordered phase at  $\phi_{\text{3MP}} = 0.09$ . Then, the number density of the solvating 3MP molecules is  $N_{\text{3MP}}^s n_{\text{salt}}$ , while that of the free 3MP molecules is  $n_{\text{3MP}} - N_{\text{3MP}}^s n_{\text{salt}}$ . In the onion phase, each onion should be composed of concentric thin membranes made of  $\text{BPh}_4^-$  ions and solvating 3MP molecules. If all the  $\text{BPh}_4^-$  ions are trapped on the membranes, the areal density of  $\text{BPh}_4^-$  is given by

$$\sigma_a = n_s d = 92 \text{ (\AA}^2\text{)}. \quad (3)$$

Here  $d = 180 \text{ \AA}$ , which is the spacing in the case (c) in Fig. 1. On both sides of each membrane,  $\text{Na}^+$  ions are localized within “counterion layers” with thickness of the order of the Debye screening length  $\lambda = (4\pi n_{\text{salt}} \ell_B)^{-1/2} \cong 15 \text{ \AA}$ , where  $\ell_B$  is the Bjerrum length in  $\text{D}_2\text{O}$  ( $\sim 7 \text{ \AA}$ ). The charge and composition segregation in this manner should much lower the solvation free energy. It is worth noting that hydrophilic and hydrophobic ions undergo microphase separation around a water-oil interface to lower the solvation free energy, largely reducing the surface tension [22].

We also argue why the lamellar structure is formed in the window composition range  $0.05 < \phi_{\text{3MP}} < 0.12$  in our system. If  $\phi_{\text{3MP}}$  is less than the lower bound, the number density of 3MP molecules should be too small to trigger the aggregation of  $\text{BPh}_4^-$  ions. If  $\phi_{\text{3MP}}$  is increased above the upper bound, 3MP molecules would

be abundant enough outside the thin membrane regions. This eventually leads to destruction of the membranes with increasing  $\phi_{\text{3MP}}$ , where delocalization of  $\text{BPh}_4^-$  ions can increase their translational entropy without penalty of the solvation free energy increase.

In summary, we have realized the onion structure in a  $\text{D}_2\text{O}$ -3MP mixture with small 3MP contents by adding a small amount of an antagonistic salt composed of hydrophilic cations and hydrophobic anions. In the previous experiments [3-6], hydrophilic salts have mostly been used and a number of unsolved controversies have been posed. As demonstrated in this Letter, the effects of adding an antagonistic salt are even more spectacular. As future experiments, we plan to measure the electric conductivity and the viscoelastic properties in salt-induced mesophases. Experiments in other soft matters in this direction should also be informative.

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